Reaction Dynamics of Radical Intermediates formed during Hydrocarbon Combustion

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The crossed molecular beams technique was utilized to explore the formation of C_5H_3 radicals via the bimolecular reactions of singlet/triplet dicarbon [$C_2(X^1\Sigma_g^+/a^3\Pi_u)$], produced via photolysis of tetrachloroethylene [$C_2Cl_4(X^1A_g)$], with 1-butyne [$C_2H_5CCH(X^1A')$] at a collision energy of 26 kJ mol^{-1}. The elusive methyl-loss pathway was detected with the resulting C_5H_3 translational energy and angular flux distributions characteristic of indirect reaction dynamics via chemically activated C_6H_6 intermediate(s) that underwent exoergic (−92 ± 16 kJ mol^{-1}) dissociation by methyl emission. This channel forms the resonantly stabilized penta-1-yn-3,4-dienyl-1 [$H_2CCCHCC(X^2A)$] radical along with the methyl radical [$CH_3(X^2A_2'')$] and is open exclusively on the triplet potential energy surface with a computed reaction energy of −86 ± 10 kJ mol^{-1}. The preferred reaction pathways proceed by barrierless addition of triplet dicarbon to the π-electronic system of 1-butyne to form methyl-bearing triplet C_6H_6 intermediates that ultimately decompose to C_5H_3 + CH_3 via a tight exit transition state. The successful unraveling of this methyl-loss channel underscores the viability of the photolytically generated dicarbon beam as an unprecedented tool to access reaction dynamics underlying the formation of resonantly stabilized free radicals that are vital to molecular mass growth processes that ultimately lead to polycyclic aromatic hydrocarbons in combustion systems.